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(54) **METHOD FOR PREPARING ACRYLIC ACID**

VERFAHREN ZUR HERSTELLUNG VON ACRYLSÄURE

PROCÉDÉ DE PRÉPARATION D'ACIDE ACRYLIQUE

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**EP 4 249 464 B1**

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**Description**

[Technical Field]

## 5 CROSS-REFERENCE TO RELATED APPLICATIONS

**[0001]** The present application claims the benefit of priority to Korean Patent Application No. 10-2021-0137936, filed on October 15, 2021.

## 10 Technical Field

**[0002]** The present invention relates to a method for preparing an acrylic acid, and more particularly, to a method for preparing an acrylic acid by a dehydration reaction of a lactic acid, which effectively removes by-products while reducing an acrylic acid loss.

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[Background Art]

**[0003]** An acrylic acid is used as a polymer raw material used in fiber, adhesives, paint, fiber processing, leather, building materials, and the like, and its demand is growing. In addition, the acrylic acid is also used as a raw material of an absorbent resin and is industrially used a lot in absorbent articles such as paper diapers and sanitary napkins, agricultural and horticultural water retaining agents, industrial water stop materials, and the like.

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**[0004]** A conventional method for preparing an acrylic acid is generally a method of oxidizing propylene in the air, but the method is a method of converting propylene into acrolein by a gaseous contact oxidation reaction and subjecting the acrolein to a gaseous contact oxidation reaction to prepare an acrylic acid, and the method produces an acetic acid as a by-product, which is difficult to separate from the acrylic acid. In addition, the method for preparing an acrylic acid using propylene uses propylene obtained by refining crude oil which is a fossil resource, as a raw material, and considering problems such as a recent rise in crude oil prices or global warming, the method has a problem in terms of raw material costs or environmental pollution.

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**[0005]** Thus, a study on a method for preparing an acrylic acid from a carbon-neutral biomass raw material was conducted. For example, there is a method for preparing an acrylic acid (AA) by a gaseous dehydration reaction of a lactic acid (LA). This method is generally a method for preparing an acrylic acid by an intramolecular dehydration reaction of a lactic acid in the presence of a catalyst at a high temperature of 300°C or higher. A reaction product including an acrylic acid is produced by the dehydration reaction of a lactic acid, and an unreacted lactic acid is included in the reaction product depending on a conversion rate. When an unreacted lactic acid is included in the reaction product, the economic feasibility of the process may be improved only by recovering the lactic acid in a separation process. However, since the lactic acid is rapidly oligomerized at a high concentration at a high temperature, it is difficult to recover the lactic acid. JP 2014 189510 A discloses a process for the dehydration of lactic acid to yield acrylic acid.

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**[Disclosure]**

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[Technical Problem]

**[0006]** An object of the present invention is to provide a method of effectively recovering an unreacted lactic acid from a reaction product produced by preparing an acrylic acid by a dehydration reaction of a lactic acid, and reusing the lactic acid, in order to solve the problems mentioned in the Background Art.

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[Technical Solution]

**[0007]** In one general aspect, a method for preparing an acrylic acid includes: dehydrating a lactic acid aqueous solution in a reaction unit to prepare a reaction product stream; passing the reaction product stream through a cooling unit and a refining unit sequentially and supplying a discharge stream from the refining unit to an acrylic acid separation column; and separating an unreacted lactic acid as a side discharge stream and separating the acrylic acid as an upper discharge stream in the acrylic acid separation column.

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## 55 [Advantageous Effects]

**[0008]** According to the method for preparing an acrylic acid of the present invention, in recovering a lactic acid from a reaction product including an acrylic acid, a recovery rate of an unreacted lactic acid may be increased by controlling the

amount of exposure time to a high temperature in a high concentration state to minimize an oligomerization reaction of a lactic acid.

[Description of Drawings]

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**[0009]**

FIG. 1 is a process flow diagram of a method for preparing an acrylic acid according to an exemplary embodiment of the present invention.

10 FIG. 2 is a process flow diagram according to a method for preparing an acrylic acid in the comparative example.

[Best Mode]

15 **[0010]** The terms and words used in the description and claims of the present invention are not to be construed limitedly as having general or dictionary meanings but are to be construed as having meanings and concepts meeting the technical ideas of the present invention, based on a principle that the inventors are able to appropriately define the concepts of terms in order to describe their own inventions in the best mode.

20 **[0011]** The term "stream" in the present invention may refer to a fluid flow in a process, or may refer to a fluid itself flowing in a pipe. Specifically, the stream may refer to both a fluid itself flowing in a pipe connecting each device and a fluid flow. In addition, the fluid may include any one or more components of gas, liquid, and solid.

**[0012]** Hereinafter, the present invention will be described in more detail for better understanding of the present invention, with reference to FIG. 1.

25 **[0013]** According to the present invention, a method for preparing an acrylic acid is provided. More specifically, the method may include: dehydrating a lactic acid aqueous solution in a reaction unit 10 to prepare a reaction product stream; passing the reaction product stream through a cooling unit 20 and a refining unit 30 sequentially and supplying a discharge stream from the refining unit 30 to an acrylic acid separation column 100; and separating an unreacted lactic acid as a side discharge stream and separating the acrylic acid as an upper discharge stream in the acrylic acid separation column 100.

30 **[0014]** Specifically, a conventional method for preparing an acrylic acid is generally a method of oxidizing propylene in the air, but the method is a method of converting propylene into acrolein by a gaseous contact oxidation reaction and subjecting the acrolein to a gaseous contact oxidation reaction to prepare an acrylic acid, and the method produces an acetic acid as a by-product, which is difficult to separate from the acrylic acid. In addition, the method for preparing an acrylic acid using propylene uses propylene obtained by refining crude oil which is a fossil resource, as a raw material, and considering problems such as a recent rise in crude oil prices or global warming, the method has a problem in terms of raw material costs or environmental pollution.

35 **[0015]** In order to solve the problems of the conventional method for preparing an acrylic acid, a study on a method for preparing an acrylic acid from a carbon-neutral biomass raw material was conducted. For example, there is a method for preparing an acrylic acid (AA) by a gaseous dehydration reaction of a lactic acid (LA). This method is generally a method for preparing an acrylic acid by an intramolecular dehydration reaction of a lactic acid in the presence of a catalyst at a high temperature. A reaction product including an acrylic acid is produced by the dehydration reaction of a lactic acid, and an unreacted lactic acid is included in the reaction product depending on a conversion rate. When an unreacted lactic acid is included in the reaction product, the economic feasibility of the process may be improved only by recovering the lactic acid in a separation process. However, since the lactic acid is rapidly oligomerized at a high concentration at a high temperature, it is difficult to recover the lactic acid.

40 **[0016]** For this, in the present invention, in order to solve the conventional problems, a method of separating a lactic acid from a reaction product including an acrylic acid prepared by the dehydration reaction of a lactic acid, in which a time that a high concentration of a lactic acid is exposed to a high temperature is shortened to prevent oligomerization of a lactic acid, thereby improving a recovery rate of an unreacted lactic acid, is to be provided.

45 **[0017]** According to an exemplary embodiment of the present invention, a lactic acid aqueous solution is supplied to the reaction unit 10 and a dehydration reaction is performed to prepare a reaction product including an acrylic acid. Here, the dehydration reaction may be performed as a gas phase reaction in the presence of a catalyst. For example, the concentration of the lactic acid in the lactic acid aqueous solution may be 10 wt% or more, 20 wt% or more, or 30 wt% or more and 40 wt% or less, 50 wt% or less, 60 wt% or less, or 70 wt% or less. When the lactic acid is present at a high concentration, oligomers such as dimers and trimers are formed by an equilibrium reaction, so that the lactic acid may be used in the form of an aqueous solution having the concentration in the above range.

50 **[0018]** The reactor may include a reactor capable of a common dehydration reaction of a lactic acid, the reactor may include a reaction tube filled with a catalyst, and while a reaction gas including volatile components of a lactic acid aqueous solution as a raw material is passed through the reaction tube, a lactic acid may be dehydrated by a gaseous contact reaction to produce an acrylic acid. The reaction gas may further include any one or more dilution gases of water vapor,

nitrogen gas, and air for adjusting a concentration, in addition to the lactic acid.

[0019] Operation conditions of the reactor may be common dehydration reaction conditions of a lactic acid. Here, the operation temperature of the reactor may refer to a set temperature of a heating medium or the like used for controlling the temperature of the reactor.

5 [0020] A catalyst used in the dehydration reaction of the lactic acid may include, for example, one or more selected from the group consisting of sulfate-based catalysts, phosphate-based catalysts, and nitrate-based catalysts. As a specific example, the sulfate may include  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{CaSO}_4$ , and  $\text{Al}_2(\text{SO}_4)_3$ , the phosphate may include  $\text{Na}_3\text{PO}_4$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{K}_3\text{PO}_4$ ,  $\text{K}_2\text{HPO}_4$ ,  $\text{KH}_2\text{PO}_4$ ,  $\text{CaHPO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{AlPO}_4$ ,  $\text{CaH}_2\text{P}_2\text{O}_7$ , and  $\text{Ca}_2\text{P}_2\text{O}_7$ , and the nitrate may include  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , and  $\text{Ca}(\text{NO}_3)_2$ . In addition, the catalyst may be supported on a support. The support may include one or more selected from the group consisting of, for example, diatomaceous earth, alumina, silica, titanium dioxide, carbides, and zeolite.

[0021] The reaction product prepared by the dehydration reaction of the lactic acid may further include water ( $\text{H}_2\text{O}$ ), gas by-products, low-boiling point by-products, high-boiling point by-products, and an unreacted lactic acid, in addition to the acrylic acid which is a desired product.

15 [0022] The method for preparing an acrylic acid by the dehydration reaction of the lactic acid may secure raw material competitiveness as compared with a conventional method of oxidizing propylene in the air and solve the problem of environmental pollution, but the conversion rate of the lactic acid is low and various by-products are produced to lower the yield of an acrylic acid. Therefore, it is necessary to develop a process for improving economic feasibility. For this, in the present invention, a method for improving economic feasibility by increasing the recovery rate of an unreacted lactic acid may be provided.

20 [0023] According to an exemplary embodiment of the present invention, the reaction product stream is passed through a cooling unit 20 and a refining unit 30 sequentially, and a discharge stream from the refining unit 30 may be supplied to an acrylic acid separation column 100 to recover a lactic acid.

[0024] According to an exemplary embodiment of the present invention, the cooling unit 20 may include one or more cooling towers, and the reaction product stream may be supplied to the cooling tower and cooled. Specifically, the reaction product prepared by the dehydration reaction of the lactic acid is a gas phase and may be condensed through the cooling tower. Gas by-products may be separated to the upper portion of the cooling tower and a liquid condensate may be discharged to the lower portion of the cooling tower, and the condensate may be supplied to the refining unit 30 at the rear end. Here, the gas by-products may include water, carbon monoxide, carbon dioxide, dilution gas, acetaldehyde, and the like as gas components.

30 [0025] According to an exemplary embodiment of the present invention, the refining unit 30 may include a water separation column and a low-boiling point separation column. For example, the water separation column may separate water from a reaction product by distillation or extraction.

[0026] When water is separated from the reaction product by extraction in the water separation column, a separate extractant is supplied to the water separation column, and the acrylic acid included in the reaction product stream may be separated as the upper discharge stream from the water separation column, using the extractant. In addition, a step for recovering the extractant may be further performed.

40 [0027] The extractant may include one or more selected from the group consisting of, for example, benzene, toluene, xylene, n-heptane, cycloheptane, cycloheptene, 1-heptene, ethylbenzene, methylcyclohexane, n-butylacetate, isobutylacetate, isobutylacrylate, n-propylacetate, isopropylacetate, methylisobutylketone, 2-methyl-1-heptene, 6-methyl-1-heptene, 4-methyl-1-heptene, 2-ethyl-1-hexene, ethylcyclopentane, 2-methyl-1-hexene, 2,3-dimethylpentane, 5-methyl-1-hexene, and isopropylbutylether. As a specific example, the extractant may be toluene.

[0028] A method of supplying the extractant to the water separation column and performing extraction may be any known method, and for example, any method such as cross current, counter current, and co-current may be used without particular limitation.

45 [0029] The reaction product stream and the extractant may be brought into contact in the water separation column, thereby separating an extract and an extraction residue solution. For example, the extract may be an acrylic acid dissolved in the extractant, and the extract may be discharged as an upper discharge stream from the water separation column. Here, the upper discharge stream from the water separation column may be supplied to a low-boiling point separation column after removing the extractant.

50 [0030] In addition, the extraction residue solution is wastewater including water and may be separated as a lower discharge stream from the water separation column. Here, aqueous by-products may be separated together with water in the lower portion of the water separation column and discharged.

55 [0031] The upper discharge stream from the water separation column is supplied to the low-boiling point separation column and low-boiling point by-products may be removed by distillation, and a reaction product from which the low-boiling point by-products have been removed may be discharged as the lower discharge stream from the low-boiling point separation column. Here, the discharge stream from the refining unit 30 supplied to the acrylic acid separation column 100 may be the lower discharge stream from the low-boiling point separation column.

**[0032]** The reaction product stream may be passed through the cooling unit 20 and the refining unit 30 sequentially to remove gas by-products, water, and low-boiling point by-products.

**[0033]** The discharge stream from the refining unit 30 may include an acrylic acid, an unreacted lactic acid, and high-boiling point by-products. The content of the unreacted lactic acid in the discharge stream from the refining unit 30 varies with the conversion rate of a lactic acid which is changed depending on the reaction and process conditions in the reaction unit 10, and for example, may be 0.5 wt% or more, 2 wt% or more, or 5 wt% or more and 10 wt% or less, 15 wt% or less, or 20 wt% or less. As such, when the unreacted lactic acid is present in the reaction product, it should be recovered or removed in a separation process, but conventionally, it was difficult to recover the unreacted lactic acid and the unreacted lactic acid was removed with high-boiling point by-products in most cases, and in the present invention, the unreacted lactic acid is recovered at a high recovery rate to improve the economic feasibility of the process.

**[0034]** According to an exemplary embodiment of the present invention, the discharge stream from the refining unit 30 may be supplied to the acrylic acid separation column 100 to recover the lactic acid. Specifically, the acrylic acid separation column 100 may be for separating the acrylic acid from the reaction product, and recovering and reusing the unreacted lactic acid.

**[0035]** The operation conditions of the acrylic acid separation column 100 may be adjusted for increasing the separation efficiency in separating each component depending on the composition of the discharge stream from the refining unit 30.

**[0036]** The operation pressure of the acrylic acid separation column 100 may be 1.3 kPa (10 torr) or more, 4.0 kPa (30 torr) or more, or 6.7 kPa (50 torr) or more and 10.7 kPa (80 torr) or less, 13.3 kPa (100 torr) or less, or 26.7 kPa (200 torr) or less. When the acrylic acid separation column 100 is operated to the operation pressure in the above range, separation efficiency in separating each of the acrylic acid, the unreacted lactic acid, and the high-boiling point by-products in the acrylic acid separation column 100 may be high and a side reaction occurring at a high temperature may be suppressed.

**[0037]** The discharge stream from the refining unit 30 may be supplied to a stage at 40% or more, 50% or more, 60% or more, or 65% or more and 80% or less, 85% or less, or 90% or less with respect to the total number of stages of the acrylic acid separation column 100. Here, the total number of stages of the acrylic acid separation column 100 may be 10 to 70. For example, when the total number of stages of the acrylic acid separation column 100 is 100, a top stage may be a 1st stage and a bottom stage may be a 100th stage, and stages at 60% to 80% of the total number of stages of the acrylic acid separation column 100 may refer to 60th to 80th stages of the acrylic acid separation column 100. A supply stage of the discharge stream from the refining unit 30 which is supplied to the acrylic acid separation column 100 is controlled to the above range, thereby increasing the separation efficiency of the acrylic acid, the lactic acid, and the high-boiling point by-products in the acrylic acid separation column 100.

**[0038]** In the acrylic acid separation column 100, the acrylic acid may be separated from the upper discharge stream, the lactic acid may be separated from the side discharge stream, and the high-boiling point by-products may be separated from the lower discharge stream.

**[0039]** The side discharge stream from the acrylic acid separation column 100 may be discharged to a stage at 20% or more, 30% or more, 50% or more, or 55% or more and 70% or less, 75% or less, or 80% or less with respect to the total number of stages of the acrylic acid separation column 100. The discharge stage of the side discharge stream from the acrylic acid separation column 100 is controlled to the above range, thereby separating a high-purity unreacted lactic acid to the side and recovering it, and thus, a time that the lactic acid is exposed to a high temperature may be minimized and a loss of a lactic acid discharged to a lower portion with the high-boiling point by-products may be minimized.

**[0040]** The content of the unreacted lactic acid included in the side discharge stream from the acrylic acid separation column 100 may be 70% or more, 70% to 90%, or 75% to 90% of the content of the unreacted lactic acid included in the discharge stream from the refining unit 30. The unreacted lactic acid separated as the side discharge stream from the acrylic acid separation column 100 may be mixed with the lactic acid aqueous solution and supplied to the reaction unit 10. The unreacted lactic acid is recovered as the side discharge stream from the acrylic acid separation column 100 and reused in the reaction unit 10, thereby improving the economic feasibility of the process.

**[0041]** The upper discharge stream from the acrylic acid separation column 100 passes through a condenser, and a part of the stream is refluxed to the acrylic acid separation column 100 and an acrylic acid may be separated from the rest of the stream. In addition, a part of the lower discharge stream from the acrylic acid separation column 100 passes through a reboiler and is refluxed to the acrylic acid separation column 100, and high-boiling point by-products may be separated to the rest of the stream.

**[0042]** A flow rate ratio of the stream passing through the reboiler and being refluxed to the acrylic acid separation column 100 to the stream being not refluxed and separating the acrylic acid in the upper discharge stream from the acrylic acid separation column 100 may be 0.8 or more, 0.85 or more, or 0.95 or more and 1.3 or less, 1.4 or less, or 1.5 or less. As described above, the flow rate ratio of the stream passing through the lower reboiler and being refluxed to the stream being not refluxed and separating the acrylic acid in the upper discharge stream from the acrylic acid separation column 100 is controlled, thereby reducing a time that the unreacted lactic acid passes through the lower reboiler of the acrylic acid separation column 100 operated at a high temperature to prevent the progress of the oligomerization reaction of the lactic acid.

[0043] According to an exemplary embodiment of the present invention, in the method for preparing an acrylic acid, if necessary, devices such as a distillation column, a condenser, a reboiler, a valve, a pump, a separator, a mixer, and the like may be further installed.

[0044] Hereinabove, the method for preparing an acrylic acid according to the present invention has been described and illustrated in the drawings, but the description and the illustration in the drawings are the description and the illustration of only core constitutions for understanding of the present invention, and in addition to the process and devices described above and illustrated in the drawings, the process and the devices which are not described and illustrated separately may be appropriately applied and used for carrying out the method for preparing an acrylic acid according to the present invention.

[0045] Hereinafter, the present invention will be described in more detail by the examples. However, the following examples are provided for illustrating the present invention, and it is apparent to a person skilled in the art that various modifications and alterations may be made without departing from the scope of the present invention

## Examples

### Example 1

[0046] According to the process flow diagram illustrated in FIG. 1, a process of preparing an acrylic acid was simulated, using an Aspen Plus simulator from Aspen Technology, Inc.

[0047] Specifically, a lactic acid aqueous solution and nitrogen (N<sub>2</sub>) as a dilution gas were supplied to a reaction unit 10 to prepare a reaction product including an acrylic acid (AA) by a dehydration reaction. The discharge stream from the reaction unit 10 including the reaction product stream was supplied to a cooling unit 20 to remove gas by-products, and the reaction product from which the gas by-products were removed was supplied to a refining unit 30. Water and low-boiling point by-products were removed from the reaction product in the refining unit 30, and a discharge stream from the refining unit 30 from which water and low-boiling point by-products were removed was supplied to a 15th stage of an acrylic acid separation column 100. At this time, the total number of stages of the acrylic acid separation column 100 was 20.

[0048] The upper discharge stream from the acrylic acid separation column 100 was passed through a condenser, and a part of the stream was refluxed to the acrylic acid separation column 100 and an acrylic acid was separated from the rest of the stream. In addition, a part of the lower discharge stream from the acrylic acid separation column 100 was passed through a reboiler and refluxed to the acrylic acid separation column 100, and high-boiling point by-products were separated from the rest of the stream. In addition, a side discharge stream including an unreacted lactic acid was separated to a 13th stage of the acrylic acid separation column 100, and the side discharge stream from the acrylic acid separation column 100 was mixed with the lactic acid aqueous solution and supplied to the reaction unit 10. At this time, a flow rate ratio of a stream passing through the reboiler and being refluxed to the acrylic acid separation column 100 to a stream being not refluxed and separating the acrylic acid in the upper discharge stream from the acrylic acid separation column 100 was controlled to 1.3.

[0049] The temperature, the pressure, and the flow rate (kg/hr) for each component in each stream are shown in the following Table 1:

[Table 1; 1 torr = 0.133 kPa]

		1	2	3	4
	<b>Temperature (°C)</b>	90	77	133	97
	<b>Pressure (torr)</b>	760	70	70	70
<b>Mass flow rate (kg/hr)</b>	Acrylic acid	1022.5	1000.0	0.0	22.5
	Lactic acid	100.0	0.0	22.1	76.0
	Lactic acid oligomer	0.0	0.0	2.0	0.0
	High-boiling point by-products	30.0	0.0	30.0	0.0
	Total	1152.5	1000.0	54.1	98.5

### Example 2

[0050] The process was performed in the same manner as in Example 1, except that the discharge stream from the refining unit 30 was supplied to a 10th stage of the acrylic acid separation column 100 and the side discharge stream including the unreacted lactic acid was separated to an 8th stage of the acrylic acid separation column 100.

**EP 4 249 464 B1**

**[0051]** At this time, the temperature, the pressure, and the flow rate (kg/hr) for each component in each stream are shown in the following Table 2:

[Table 2; 1 torr = 0.133 kPa]

5		1	2	3	4	
	<b>Temperature (°C)</b>	90	77	133	97	
	<b>Pressure (torr)</b>	760	70	70	70	
10	<b>Mass flow rate (kg/hr)</b>	Acrylic acid	1022.5	999.6	0.0	22.9
		Lactic acid	100.0	0.4	22.1	75.6
		Lactic acid oligomer	0.0	0.0	2.0	0.0
15		High-boiling point by-products	30.0	0.0	30.0	0.0
		Total	1152.5	1000.0	54.1	98.5

**Comparative Examples**

20 **Comparative Example 1**

**[0052]** According to the process flow diagram illustrated in FIG. 2, a process of preparing an acrylic acid was simulated, using an Aspen Plus simulator from Aspen Technology, Inc.

25 **[0053]** Specifically, a lactic acid aqueous solution and nitrogen (N<sub>2</sub>) as a dilution gas were supplied to a reaction unit 10 to prepare a reaction product including an acrylic acid (AA) by a dehydration reaction. The discharge stream from the reaction unit 10 including the reaction product stream was supplied to a cooling unit 20 to remove gas by-products, and the reaction product from which the gas by-products were removed was supplied to a refining unit 30. Water and low-boiling point by-products were removed from the reaction product in the refining unit 30, and a discharge stream from the refining unit 30 from which water and low-boiling point by-products were removed was supplied to a 3rd stage of an acrylic acid separation column 100. At this time, the total number of stages of the acrylic acid separation column 100 was 10.

30 **[0054]** The upper discharge stream from the acrylic acid separation column 100 was passed through a condenser, and a part of the stream was refluxed to the acrylic acid separation column 100 and an acrylic acid was separated from the rest of the stream. In addition, a part of the lower discharge stream from the acrylic acid separation column 100 was passed through a reboiler and refluxed to the acrylic acid separation column 100, and high-boiling point by-products and an unreacted lactic acid were separated from the rest of the stream and supplied to a lactic acid recovery column 200.

35 **[0055]** The upper discharge stream from the lactic acid recovery column 200 was passed through a condenser, and a part of the stream was refluxed to the lactic acid recovery column 200 and the unreacted lactic acid was recovered from the rest of the stream. In addition, a part of the lower discharge stream from the lactic acid recovery column 200 was passed through a reboiler and refluxed to the lactic acid recovery column 200, and high-boiling point by-products were separated from the rest of the stream. The lactic acid recovered from the upper discharge stream from the lactic acid recovery column 200 was mixed with the lactic acid aqueous solution and supplied to the reaction unit.

40 **[0056]** The temperature, the pressure, and the flow rate (kg/hr) for each component in each stream are shown in the following Table 3:

[Table 3; 1 torr = 0.133 kPa]

45		1	2	3	4	5	
	<b>Temperature (°C)</b>	90	90	117	97	133	
	<b>Pressure (torr)</b>	760	120	120	70	70	
50	<b>Mass flow rate (kg/hr)</b>	Acrylic acid	1022.5	998.1	24.4	24.4	0.0
		Lactic acid	100.0	1.9	96.1	72.6	21.6
		Lactic acid oligomer	0.0	0.0	2.0	0.0	3.9
55		High-boiling point by-products	30.0	0.0	30.0	0.0	30.0
		Total	1152.5	1000.0	152.5	97.0	55.5

**[0057]** Referring to Tables 1 to 3, in Examples 1 and 2 in which the unreacted lactic acid was recovered from the reaction product by the method for preparing an acrylic acid according to the present invention, it was confirmed that the purity of the acrylic acid was 99.9% to 100%, and the recovery rate of the lactic acid was 75% or more. In particular, in Example 1 in which the supply stage of the discharge stream from the refining unit 30 was controlled to a stage at 65% to 85% of the total number of stages of the acrylic acid separation column 100, the discharge stage of the side discharge stream from the acrylic acid separation column 100 was controlled to a stage at 55% to 75%, and the flow rate ratio of the stream passing through the reboiler and being refluxed to the acrylic acid separation column 100 to the stream being not refluxed and separating the acrylic acid in the upper discharge stream from the acrylic acid separation column 100 was controlled to 1 to 1.5, it was confirmed that the purity of the acrylic acid reached 100%, and the recovery rate of the lactic acid was higher.

**[0058]** In comparison, in Comparative Example 1, which was conventionally arbitrarily designed for recovering the unreacted lactic acid discharged with the high-boiling point by-products in the lower portion of the acrylic acid separation column 100, the lower discharge stream from the acrylic acid separation column 100 was supplied to the lactic acid separation column at the rear end and the lactic acid was recovered in the lactic acid separation column, thereby increasing the amount of exposure time to a high temperature in a high concentration state to increase an equilibrium reaction rate, for example, discharging the high concentration of the unreacted lactic acid at a high temperature from the lower portion of the acrylic acid separation column 100 and heating the unreacted lactic acid again in the column at the rear end, and thus, the oligomerization reaction of a lactic acid was promoted to lower the recovery rate of the unreacted lactic acid, and additional energy was used.

## Claims

1. A method for preparing an acrylic acid, the method comprising:

dehydrating a lactic acid aqueous solution in a reaction unit to prepare a reaction product stream;  
passing the reaction product stream through a cooling unit and a refining unit sequentially and supplying a discharge stream from the refining unit to an acrylic acid separation column; and  
separating an unreacted lactic acid as a side discharge stream and separating the acrylic acid as an upper discharge stream in the acrylic acid separation column.

2. The method for preparing an acrylic acid of claim 1, wherein the discharge stream from the refining unit is supplied to a stage at 40% to 90% with respect to the total number of stages of the acrylic acid separation column.

3. The method for preparing an acrylic acid of claim 1, wherein the discharge stream from the refining unit is supplied to a stage at 65% to 85% with respect to the total number of stages of the acrylic acid separation column.

4. The method for preparing an acrylic acid of claim 1, wherein the side discharge stream from the acrylic acid separation column is discharged from a stage at 20% to 80% respect to the total number of stages of the acrylic acid separation column.

5. The method for preparing an acrylic acid of claim 1, wherein the side discharge stream from the acrylic acid separation column is discharged from a stage at 55% to 75% respect to the total number of stages of the acrylic acid separation column.

6. The method for preparing an acrylic acid of claim 1, wherein an operation pressure of the acrylic acid separation column is 1.3 kPa (10 torr) to 26.7 kPa (200 torr).

7. The method for preparing an acrylic acid of claim 1, wherein a flow rate ratio of a stream passing through a reboiler and being refluxed to the acrylic acid separation column to a stream being not refluxed and separating the acrylic acid in the upper discharge stream from the acrylic acid separation column is 0.8 to 1.5.

8. The method for preparing an acrylic acid of claim 1, wherein the unreacted lactic acid separated as the side discharge stream from the acrylic acid separation column is mixed with the lactic acid aqueous solution and supplied to the reaction unit.

9. The method for preparing an acrylic acid of claim 1, wherein high-boiling point by-products are separated from a lower discharge stream from the acrylic acid separation column.

10. The method for preparing an acrylic acid of claim 1, wherein the reaction product stream includes the acrylic acid, water, gas by-products, low-boiling point by-products, high-boiling point by-products, and the unreacted lactic acid.
- 5 11. The method for preparing an acrylic acid of claim 10, wherein the cooling unit removes the gas by-products from the reaction product stream and the refining unit removes water and the low-boiling point by-products from the reaction product stream.

### Patentansprüche

- 10 1. Verfahren zur Herstellung einer Acrylsäure, wobei das Verfahren umfasst:

15 Dehydrieren einer wässrigen Milchsäurelösung in einer Reaktionseinheit, um einen Reaktionsproduktstrom herzustellen,  
Durchleiten des Reaktionsproduktstroms nacheinander durch eine Kühleinheit und eine Raffinationseinheit und  
Zuführen eines Abflussstroms aus der Raffinationseinheit zu einer Acrylsäure-Trennsäule und  
Abtrennen einer nichtumgesetzten Milchsäure als Seitenabflussstrom und Abtrennen der Acrylsäure als ein  
oberer Abflussstrom in der Acrylsäure-Trennsäule.

- 20 2. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei der Abflussstrom aus der Raffinationseinheit einer Stufe bei 40 % bis 90 % in Bezug auf die Gesamtstufenzahl der Acrylsäure-Trennsäule zugeführt wird.

- 25 3. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei der Abflussstrom aus der Raffinationseinheit einer Stufe bei 65 % bis 85 % in Bezug auf die Gesamtstufenzahl der Acrylsäure-Trennsäule zugeführt wird.

- 30 4. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei der Seitenabflussstrom aus der Acrylsäure-Trennsäule aus einer Stufe von 20 % bis 80 % in Bezug auf die Gesamtstufenzahl der Acrylsäure-Trennsäule abgeleitet wird.

- 35 5. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei der Seitenabflussstrom aus der Acrylsäure-Trennsäule aus einer Stufe von 55 % bis 75 % in Bezug auf die Gesamtstufenzahl der Acrylsäure-Trennsäule abgeleitet wird.

- 40 6. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei der Betriebsdruck der Acrylsäure-Trennsäule 1,3 kPa (10 Torr) bis 26,7 kPa (200 Torr) beträgt.

- 45 7. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei ein Durchflussverhältnis eines Stroms, der durch einen Reboiler läuft und zur Acrylsäure-Trennsäule zurückgeführt wird, zu einem Strom, der nicht zurückgeführt wird und die Acrylsäure in dem oberen Abflussstrom aus der Acrylsäure-Trennsäule abtrennt, 0,8 bis 1,5 beträgt.

- 50 8. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei die nichtumgesetzte Milchsäure, die als Seitenabflussstrom aus der Acrylsäure-Trennsäule abgetrennt wird, mit der wässrigen Milchsäurelösung gemischt und der Reaktionseinheit zugeführt wird.

- 55 9. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei hochsiedende Nebenprodukte von einem unteren Abflussstrom aus der Acrylsäure-Trennsäule abgetrennt werden.

10. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 1, wobei der Reaktionsproduktstrom die Acrylsäure, Wasser, Gasnebenprodukte, niedrigsiedende Nebenprodukte, hochsiedende Nebenprodukte und die nichtumgesetzte Milchsäure einschließt.

11. Verfahren zur Herstellung einer Acrylsäure nach Anspruch 10, wobei die Kühleinheit die Gasnebenprodukte aus dem Reaktionsproduktstrom entfernt und die Raffinationseinheit Wasser und die niedrigsiedende Nebenprodukte aus dem Reaktionsproduktstrom entfernt.

**Revendications**

1. Procédé de préparation d'acide acrylique, le procédé comprenant :

5 la déshydratation d'une solution aqueuse d'acide lactique dans une unité de réaction pour préparer un courant de produit de réaction ;  
le passage du courant de produit de réaction à travers une unité de refroidissement et une unité de raffinage séquentiellement et la fourniture d'un courant de décharge provenant de l'unité de raffinage à une colonne de séparation d'acide acrylique ; et  
10 la séparation d'un acide lactique n'ayant pas réagi en tant qu'un courant de décharge latéral et la séparation de l'acide acrylique en tant qu'un courant de décharge supérieur dans la colonne de séparation d'acide acrylique.

2. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel le courant de décharge provenant de l'unité de raffinage est fourni à un étage à 40 % à 90 % par rapport au nombre total d'étages de la colonne de séparation d'acide acrylique.  
15

3. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel le courant de décharge provenant de l'unité de raffinage est fourni à un étage à 65 % à 85 % par rapport au nombre total d'étages de la colonne de séparation d'acide acrylique.  
20

4. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel le courant de décharge latéral provenant de la colonne de séparation d'acide acrylique est déchargé à partir d'un étage à 20 % à 80 % par rapport au nombre total d'étages de la colonne de séparation d'acide acrylique.

25 5. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel le courant de décharge latéral provenant de la colonne de séparation d'acide acrylique est déchargé à partir d'un étage à 55 % à 75 % par rapport au nombre total d'étages de la colonne de séparation d'acide acrylique.

30 6. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel une pression de fonctionnement de la colonne de séparation d'acide acrylique est 1,3 kPa (10 torr) à 26,7 kPa (200 torr).

7. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel un rapport de débit d'un courant passant à travers un rebouilleur et étant reflué vers la colonne de séparation d'acide acrylique à un courant n'étant pas reflué et séparant l'acide acrylique dans le courant de décharge supérieur provenant de la colonne de séparation d'acide acrylique est 0,8 à 1,5.  
35

8. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel l'acide lactique n'ayant pas réagi séparé en tant que le courant de décharge latéral provenant de la colonne de séparation d'acide acrylique est mélangé avec la solution aqueuse d'acide lactique et fourni à l'unité de réaction.  
40

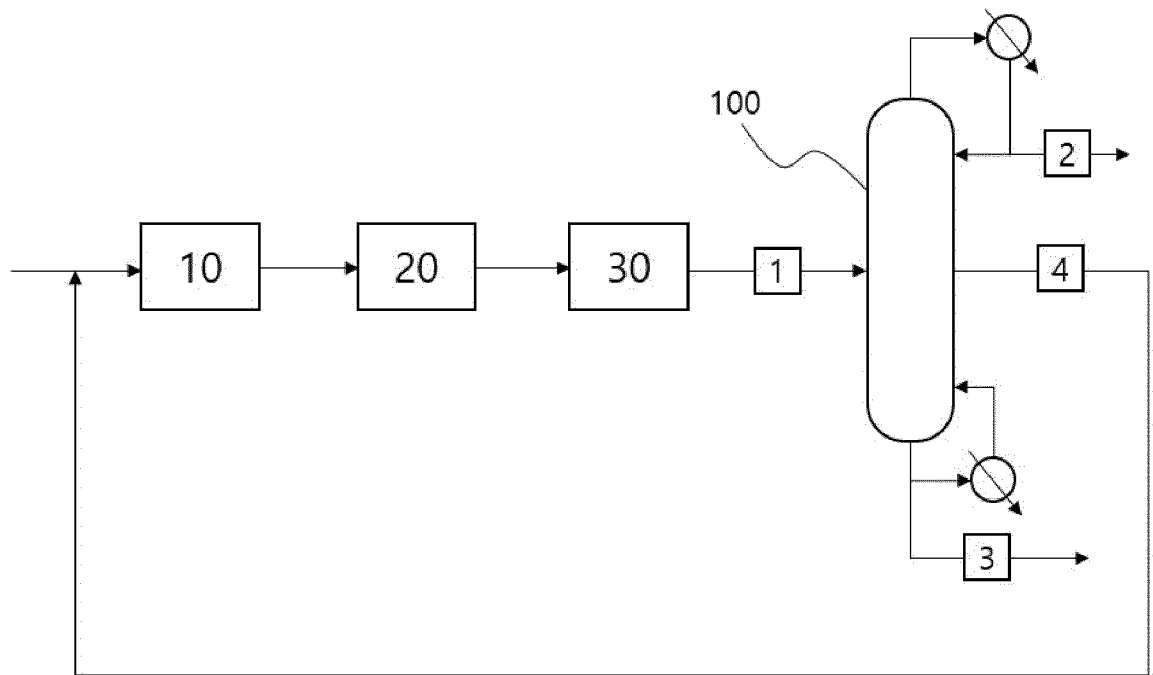
9. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel des sous-produits à point d'ébullition haut sont séparés d'un courant de décharge inférieur provenant de la colonne de séparation d'acide acrylique.

45 10. Procédé de préparation d'acide acrylique selon la revendication 1, dans lequel le courant de produit de réaction inclut l'acide acrylique, l'eau, des sous-produits gazeux, des sous-produits à point d'ébullition bas, des sous-produits à point d'ébullition haut, et l'acide lactique n'ayant pas réagi.

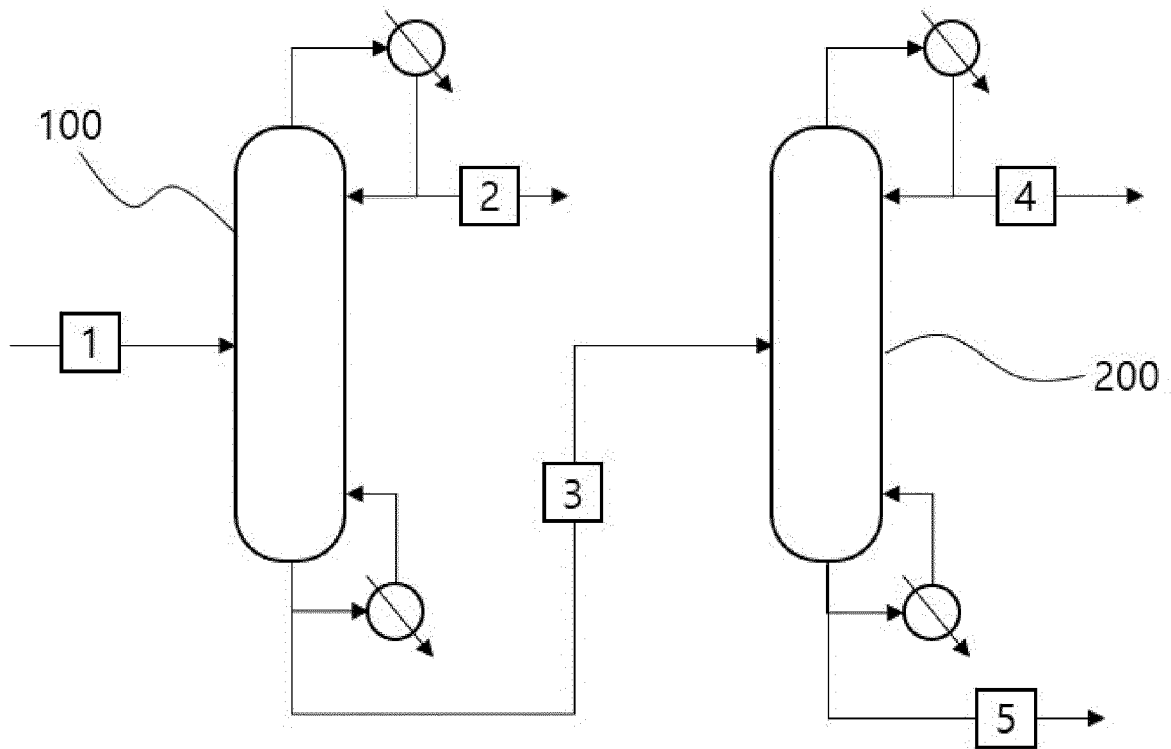
50 11. Procédé de préparation d'acide acrylique selon la revendication 10, dans lequel l'unité de refroidissement élimine les sous-produits gazeux du courant de produit de réaction et l'unité de raffinage élimine l'eau et les sous-produits à point d'ébullition bas du courant de produit de réaction.

55

【FIG. 1】



【FIG. 2】



**REFERENCES CITED IN THE DESCRIPTION**

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